Effect of Zeta Potential on Perchlorate Rejection by Negatively Charged Nanofiltration Membranes

Yeomin Yoon
University of Colorado at Boulder
Boulder, CO

Gary Amy
University of Colorado at Boulder
Boulder, CO

Sun Liang
Metropolitan Water District of Southern California
La Verne, CA

Introduction

With the recent emergence of perchlorate (ClO_4^-) contamination as an important drinking water quality issue, given that ClO_4^- can interfere with the human thyroid gland's capability to utilize iodine in the production of growth and development hormones, studies have been performed to assess removal of ClO_4^- by membrane technology. The California Department of Health Services (CDHS) has defined a provisional action level of 18 μg/L.

Several streaming potential measurement studies have been performed to determine the effect of solution chemistry of the surface charge of reverse osmosis (RO), nanofiltration (NF), and ultrafiltration (UF) membranes (Childress and Elimelech, 1996; Causserand et. al., 1994; Chen et. al., 1994)

Several NF and UF studies have been performed to evaluate removal of anions such as nitrate and arsenate that are physically/chemically similar (e.g., molecular mass (MM) and charge) to perchlorate. One study showed the effect of pH on rejection of different species of arsenic by nanofiltration (Urase et. al., 1998). Studies by Brandhuber and Amy (1998) on treatment of surface and ground waters with a variety of RO, NF, and UF membranes have indicated that anionic As (V) is consistently better rejected than nonionic As (III). Another study has also shown that nitrate is easily removed by cellulose acetate membranes when small concentrations of cationic surfactant are added (Morel et. al., 1997).

In this study, two NF membranes, ESNA and MX07, which have similar chemistry based on material and different nominal relative molecular mass cutoffs (MMCOs), have been compared in terms of the effects of membrane surface charge, as affected by solution pH and conductivity, on perchlorate rejection. To facilitate comparison, the ratio of the *initial* pure water flux (J_o) to the estimated boundary layer back-diffusional mass transfer coefficient (k), (J_o/k), was used to define similar *initial* hydrodynamic operating conditions for the two different membrane evaluated.

Exclusion of ClO_4^- by membranes possessing a negative charge can be explained by basic transport equations based on diffusion and convection. Another equation, the Donnan Equilibrium equation, can explain ClO_4^- exclusion by negatively charged membranes. If ClO_4^- rejection is controlled by those equations, the following predictions can be made: i) ClO_4^- rejection will increase with negatively increasing membrane charge associated with increasing pH, ii) ClO_4^- rejection will decrease with increasing ionic strength, and iii) ClO_4^- rejection will

be influenced by the presence of other mono- and multivalent cations (counter-ions) and anions (co-ions) in solution. A cross-flow flat-sheet membrane unit for NF membranes was employed for experiments to test these predictions.

Materials and Methods
Flat-sheet test unit

An Osmonics SEPA flat-sheet test cell was employed for experiments. This cell permits testing of a single of 9.25 cm × 14.6 cm membrane coupon under cross flow conditions. The feed solution was drawn from a 4-L reservoir, and supplied to the flat sheet tester. The retentate and permeate streams were returned to the reservoir after passing through the test cell. The temperature of the feed solution was maintained at ± 1.0 °C of the desired temperature by immersing the reservoir in a temperature controlled water bath. The feed pressure, and retentate and permeate flow rates were monitored. The feed flow rate was calculated from the measured retentate and permeate flow rates.

k can be estimated by correlation (Poter, 1972) for laminar flow in a rectangular channel:

$$k = 1.62 \left(\frac{UD^2}{d_h L} \right)^{0.33} (cm/s) \qquad (1)$$

Where U is the average cross-flow velocity of feed fluid (cm/s), D is the diffusion coefficient (cm^2/s), d_h is equivalent hydraulic diameter (cm), and L is channel length (cm). In this study, all of the experiments were performed at a J_o/k ratio of 0.6 for ClO_4^- rejection tests.

Streaming potential measurements

Streaming potential was measured with an electrokinetic analyzer apparatus (EKA). The electrolyte solution was held in a jacketed reservoir kept at constant temperature with water circulated through a heating and cooling water bath. The external pH and conductivity sensors were placed in the electrolyte reservoir. Conductivity, temperature, pressure, and streaming potential were monitored with internal sensors.

The Helmholtz-Smoluchowski equation has been used to calculate the zeta potential.

$$\zeta = \frac{\Delta U \cdot \eta \cdot L}{\Delta P \cdot \varepsilon \varepsilon_0 \cdot A \cdot R} \qquad (2)$$

where ζ is zeta potential (mV), $\Delta U/\Delta P$ is the change in streaming potential with pressure (mV Pa^{-1}), η is the viscosity of the solution (Pa s), L is the channel length (m), ε_0 is the permittivity of free space (m^{-1} Ω^{-1}), ε is the dielectric constant of the solution, A is the cross-sectional area (m^2), and R is the ohmic resistance of the electrolyte and channel (Ω).

It is assumed that the electrolyte solution, with conductivity k, carries most of the current and is used as an approximation of L A^{-1} R^{-1} for ionic solutions > 10^{-3} M. This approximation is acceptable for the membrane materials evaluated and results in the following simplification where k is the specific conductance:

$$\zeta = \frac{\Delta U \cdot \eta \cdot \kappa}{\Delta P \cdot \varepsilon \varepsilon_0} \tag{3}$$

Membrane properties

Table 1 shows the physical/chemical properties of membranes used for this study. The ESNA and MX07 membranes were NF types based on their nominal MMCO. Both membranes possessed a negative surface charge at pH 8 and conductivity 115 mS/m based on their zeta potential.

Table 1. Membrane properties

Membrane	Manufacturer	Material	MMCO	PWP (L/m²-day-kPa)	ZP at pH 8 and conductivity 115 mS/m
ESNA	Hydranautics	Polyamide TFC	200	1.05	- 43.2 mV
MX07	Osmonics	Polyamide TFC	400	0.47	- 41.3 mV

Membrane Preparation

For the streaming potential measurements, membrane samples were cut to fit the measurement cell and then wetted in KCl solution at the desired pH and stored in a refrigerator for the soaking time specified in the experimental design.

For the cross-flow flat-sheet tests, membrane test coupons were prepared from a single element provided by the membrane manufacturer. Each membrane coupon was soaked for at least 24 hours in pure water (deionized organic free water) prior to testing. Before testing, the membrane coupon was flushed with pure water until the membrane was stable in terms of pure water permeability. A new membrane coupon was used for each experiment.

Experimental solution preparation, protocol, and perchlorate analysis

The desired experimental solutions were prepared by spiking 20-L of pure water with the desired concentration of ClO_4^-. From the 20-L stock solution, 4-L volumes were drawn and spiked to the desired concentration of co-ion, counterion, or other conditions planned for the individual experiment.

With the solutions prepared above, individual experiments were performed over a 2-hour period with the objective of determining perchlorate rejection. Samples of each stream (feed, retentate, permeate) were taken for mass balance calculation to verify the measurement of perchlorate concentrations. Perchlorate was measured by a Dionex Model DX300 Ion Chromatograph (IC) with a lower detection limit of 4 µg/L. Samples were stored in a 4 °C refrigerator and generally analyzed within 10 days.

Results

Figure 1 shows the effect of pH on membrane charge, based on ZP, and perchlorate rejection for the two membranes, NF, ESNA and MX07, when 100 µg/L (10^{-6} M) of ClO_4^- was spiked into a 0.0025 M (30 mS/m) KCl solution to prepare a feed solution. The pH of the feed solution was controlled by adding HCl and/or KOH. From the results, a few generalizations can be made regarding the polyamide TFC membranes. The membrane charge of the two NF membranes (negatively) increased with increasing pH. ClO_4^- rejection increased with increasing ZP of the membranes, which verified that ClO_4^- rejection was influenced by electrostatic

interactions with the membranes. However, the membranes showed different ClO_4^- rejection increases, 70 % to 90 % for ESNA and 40 % to 70 % for MX07, with increasing pH. The results indicate that the ESNA membrane was affected by electrostatic interaction less than the MX07 membrane. It is assumed that the steric (size) exclusion mechanism was more dominant for the ESNA membrane since the ESNA membrane has a have smaller membrane pore size than the MX07 membrane based on their MMCOs.
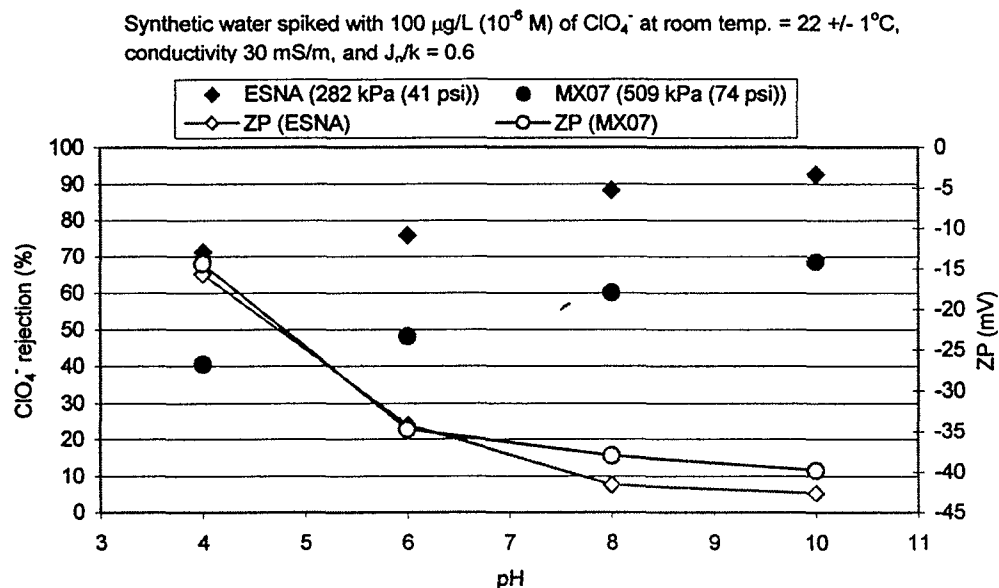
Synthetic water spiked with 100 µg/L (10^{-6} M) of ClO_4^- at room temp. = 22 +/- 1°C, conductivity 30 mS/m, and J_v/k = 0.6

Figure 1 Effect of pH on zeta potential and perchlorate rejection for NF (ESNA and MX07) membranes

For the ionic strength experiment, KCl was added to a feed solution of 100 µg/L ClO_4^- to prepare the three different desired levels, 0.0025 M (30 mS/m), 0.005 M (60 mS/m), and 0.01 M (115 mS/m); pH was adjusted to 8.0 by adding HCl and/or KOH. ZP was calculated based on streaming potential measurements at three different conductivity levels. Figure 2 plots the effect of ionic strength on zeta potential and perchlorate rejection for the ESNA and MX07 membranes.

The charge of the membranes (negatively) increased slightly with increasing ionic strength. An increasing concentration of KCl resulted in a slight decrease in perchlorate rejection for the ESNA membrane, and a significant reduction of perchlorate rejection for the MX07 membrane.

Synthetic water spiked with 100 µg/L (10^{-6} M) of ClO_4^- at room temp. = 22 +/- 1°C, pH 8.0, and J_o/k = 0.6
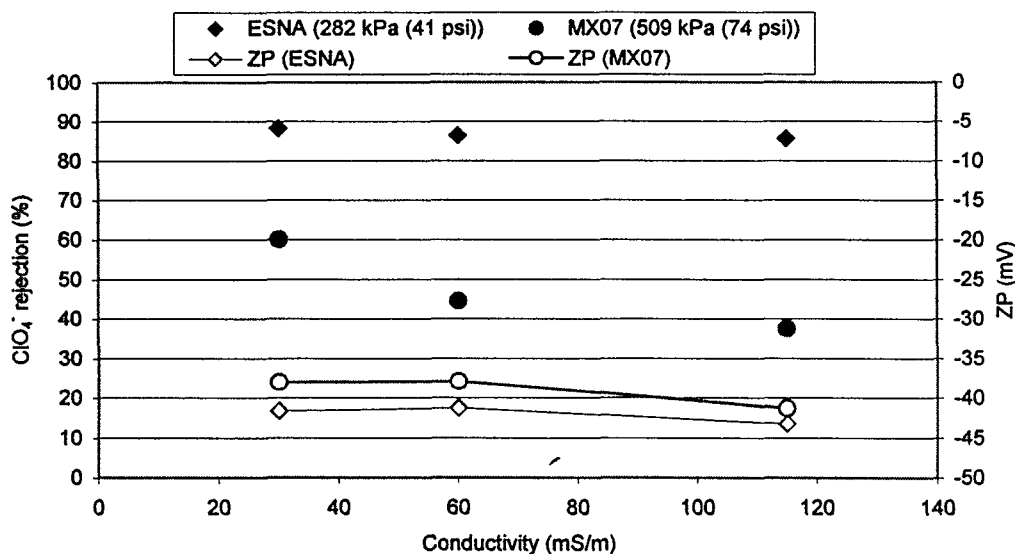

Figure 2 Effect of solution conductivity on zeta potential and perchlorate rejection
for NF (ESNA and MX07) membranes

Monovalent and divalent anions, Cl^- and SO_4^{2-}, were added to the perchlorate feed solution in the presence of a common counter-ion (Na^+). The experiments were performed at pH 8.0. Figures 3 and 4 plot the effect of co-ion concentration on perchlorate rejection for the ESNA and MX07 membranes. Perchlorate rejection slightly decreased for the ESNA membrane and significantly decreased for the MX07 membrane with increasing co-ion concentration.

Figures 5 and 6 show the effect of varying counter-ion concentration on perchlorate rejection for the ESNA and MX07 membranes. In this experiment, mono- and divalent cations, Na^+, Mg^{2+}, and Ca^{2+}, were added to the perchlorate feed solution in the presence of a common co-ion (Cl^-) at pH 8.0. Increasing concentrations of counter-ions resulted in a slight decrease in perchlorate rejection for the ESNA membrane and a significant decrease for the MX07 membrane.

From the results shown in Figures 3 through 6, it is asserted that the ESNA membrane was mostly influenced by steric (size) exclusion and electrostatic interaction was more significant for the MX07 membrane in terms of perchlorate rejection.
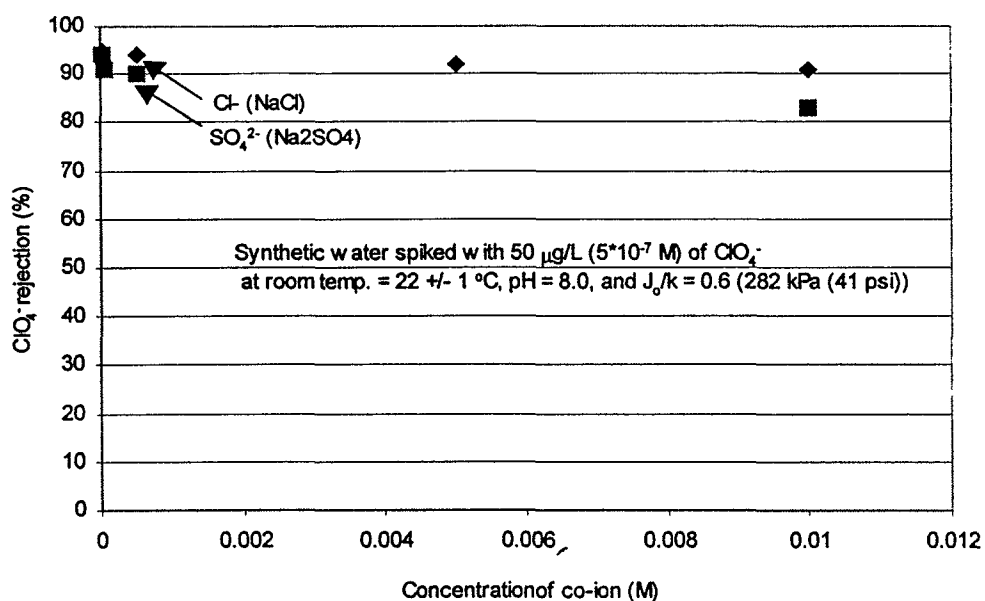
Figure 3 Effect of mono- and divalent counter-ions on perchlorate rejection for a
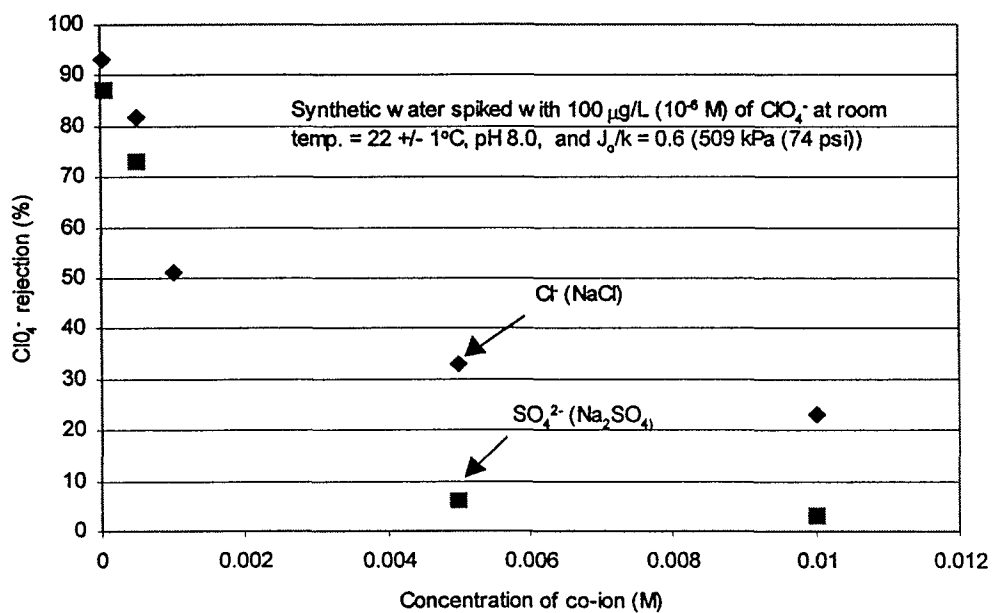NF (ESNA) membrane

Figure 4 Effect of mono- and divalent co-ions on perchlorate rejection for a NF
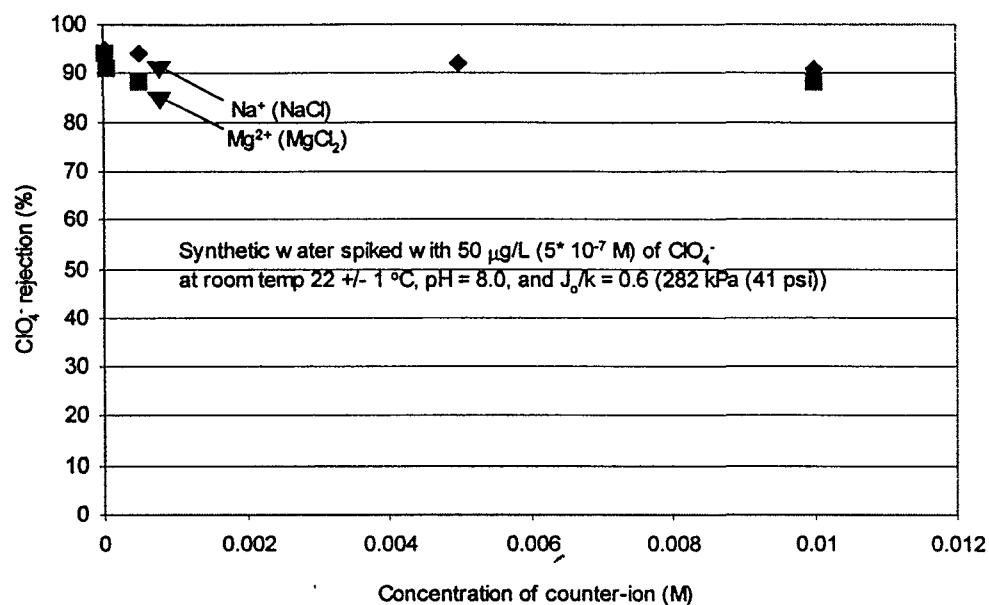(MX07) membrane

Figure 5 Effect of mono- and divalent counter-ions on perchlorate rejection for a
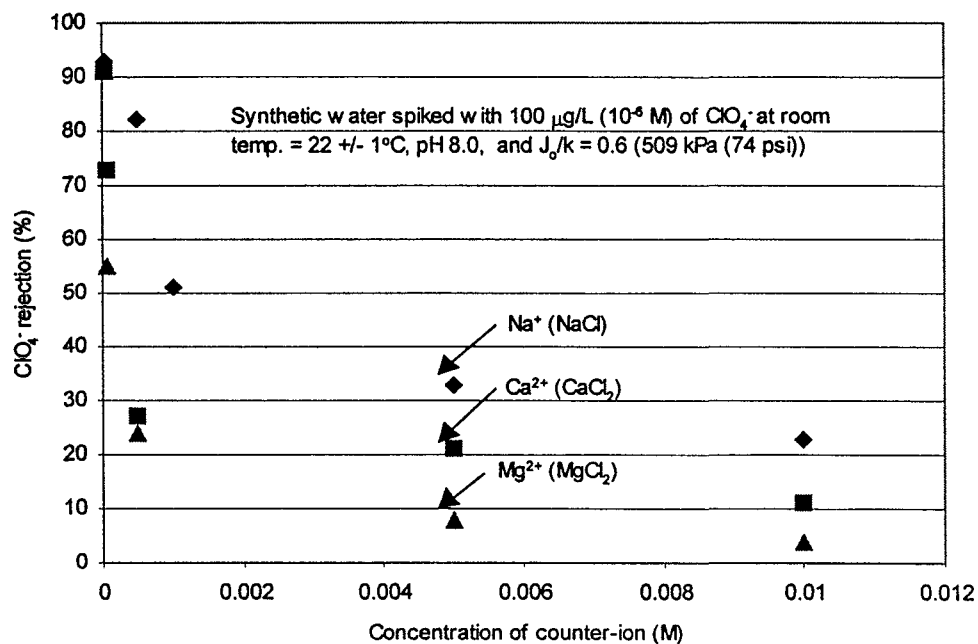NF (ESNA) membrane

Figure 6 Effect of mono- and divalent counter-ions on perchlorate rejection for a
NF (MX07) membrane

Conclusions

It was found that ZP, derived from streaming potential measurements, was useful to describing the transport phenomenon of an anion, perchlorate, through negatively charged NF membranes. Cross flow flat-sheet experiments for perchlorate rejection by negatively charged NF membranes demonstrated the following trends:

- ClO_4^- rejection improved with (negatively) increasing ZP associated with increasing pH;
- ClO_4^- rejection decreased with increasing ionic strength of the solution;
- ClO_4^- rejection was reduced by the presence of mono- and divalent anions;
- ClO_4^- rejection was reduced by the presence of mono- and divalent cations.

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